

Structural and Magnetic Study of Zr⁴⁺ Substituted Magnesium Ferrite Nano-particles

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ABSTRACT

Nano-sized Zr-Al doped magnesium ferrites with nominal composition, Mg (1+x)Zr_x(FeAl)_{1-x}O₄ (x = 0.2, 0.4, 0.6, 0.8) were synthesized using sol-gel auto combustion. The structural study of the synthesized iron oxide samples were carried out by X-ray diffraction (XRD). The XRD analysis confirmed face centered cubic structure for all the compositions of Mg(1+x)Zr_x(FeAl)_{1-x}O₄ nanocrystallites. The variation in lattice parameter as determined by XRD data agreed with variation of ionic radii of host cations Zr⁴⁺ and Al³⁺. Characterized spinel nano-ferrites were evaluated for their potential applications by magnetic hysteresis loops. Value of saturation magnetization (M_s) goes on increased up to x = 0.8 with fluctuations in between x = 0.2 to x = 0.8. The values of M_s of some compositions predicted the potential applications in field of hyperthermia, recording media and microwave devices.

Keywords: Spinel ferrite, Structural, magnetic superparamagnetic, etc.

1. Introduction

Spinel ferrite, having chemical composition Mg_(1+x)Zr_x(FeAl)_{1-x}O₄ (x = 0.2, 0.4, 0.6, 0.8) has a face-centered cubic system with large unit cell containing eight formula units [1]. In the system of spinel ferrite there are two kinds of lattice sites for occupancy of cations in A and B sites having tetrahedral and octahedral co-ordinations, respectively [2]. Generally, the M²⁺ and Fe³⁺ cations are distributed at both the sites normally the M²⁺ at tetrahedral site and Fe³⁺ at octahedral site. [3]. The variation of cation distribution over the A and B sites leads to different magnetic, electric properties etc, it has been well-known that the cation distribution in nano-crystalline ferrites is different from that in the bulk ferrites [4][5]. Therefore characteristics of the nano-ferrites can be explained on the basis of the dependence of cation distribution, method of preparation, sintering temperature, particle size etc. The information for the lattice structure of spinel ferrite provides outstanding opportunities to understanding the chemical influences on super-paramagnetic properties of nanoparticles [6]. For the better applications of nano-materials in various fields [7], we need new materials to be designed and exploited of more predictable

properties than what are currently available. Super paramagnetic iron oxide nanoparticles, having low Curie temperature, is used in biomedical appliances as it causes the materials to demagnetized when the applied magnetic field is turned off, it found that substitution of Zr^{4+} ion strongly affected on the saturation magnetization as well as hysteresis loop in spinel ferrite [8].

2. Experimental

2.1. Materials

The raw materials used for sol-gel auto combustion synthesis of $Mg_{(1+x)}Zr_x(FeAl)_{1-x}O_4$ ($x = 0.2, 0.4, 0.6, 0.8$) nanoparticles were magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), zirconium nitrate ($ZrO(NO_3)_2$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), Urea ($NH_2-CO-NH_2$). All the reagents used for the synthesis of cobalt ferrite nanoparticles were analytical grade.

2.2. Synthesis

$Mg_{(1+x)}Zr_x(FeAl)_{1-x}O_4$ ($x = 0.2, 0.4, 0.6, 0.8$) nanoparticles were synthesized by sol-gel auto combustion method using urea as a fuel. The stoichiometric proportions of metal nitrates to fuel (urea) ratio was taken into separate borosil glass beakers. These were stirred for 15-20 minutes to dissolve completely into distilled water. After complete dissolution they were mixed together. Then the solution was constantly magnetically stirred and heated at 80-90 °C for 6 h on a hot plate. On the formation of viscous gel, then the gel were kept in microwave oven for instant fire at 600 watt. The dried gel started and finally powder was obtained. The as prepared ferrite powder was grinded for 4 hrs and annealed at 800 °C for 4 hrs in muffle furnace.

2.3. Characterizations

In the present work, zirconium and aluminum substituted magnesium ferrite samples were synthesized by sol-gel auto combustion method and characterized by X-ray diffraction technique and vibrating sample magnetometer. X-ray diffraction patterns of all the samples were recorded in the 2θ range 20° to 80° with scanning rate of 2° per minute using Cu-K α radiation of wavelength 1.5406 Å. The effect of substitution on the magnetic properties like saturation magnetization (MS), remanence (Mr) and coercivity (HC) was studied using a Vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. XRD(x-ray diffraction)

Fig: 1 shows the x-ray diffraction pattern of the sintered Zr-Al substituted magnesium ferrite samples, from the (hkl) planes (111), (200), (311), (222), (422), (511) and (400) confirming the cubic spinel structure [9]. The other peaks in the XRD pattern gives evidence for the existence of an extra phase of ZrO_2 [10]. It has been observed from the x-ray diffraction pattern, as the value of "x" increases from $x = 0.2$ to $x = 0.8$ the intensity peaks of ZrO_2 increases. This may be due to the effect of increase in concentration of Zr^{4+} ions in the samples [11].

An overall increase in lattice parameter (from 8.5686 Å for $x = 0.2$ to 8.8169 Å for $x = 0.8$) as shown in fig. 2 due to large ionic radius of Zr (0.72 Å) as compare to Fe (0.64 Å) [12], [13]. Zr^{4+} ions are known to occupy tetrahedral (A) sites due to their

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strong preference for tetrahedral coordination [14] and Fe^{3+} ions do not have the sufficient occupancy in the cubic system of tetrahedral (A) site. Similarly Al^{3+} has its occupancy in the octahedral (B) site therefore the intensity of all the (hkl) planes of this cubic system gradually decreases.

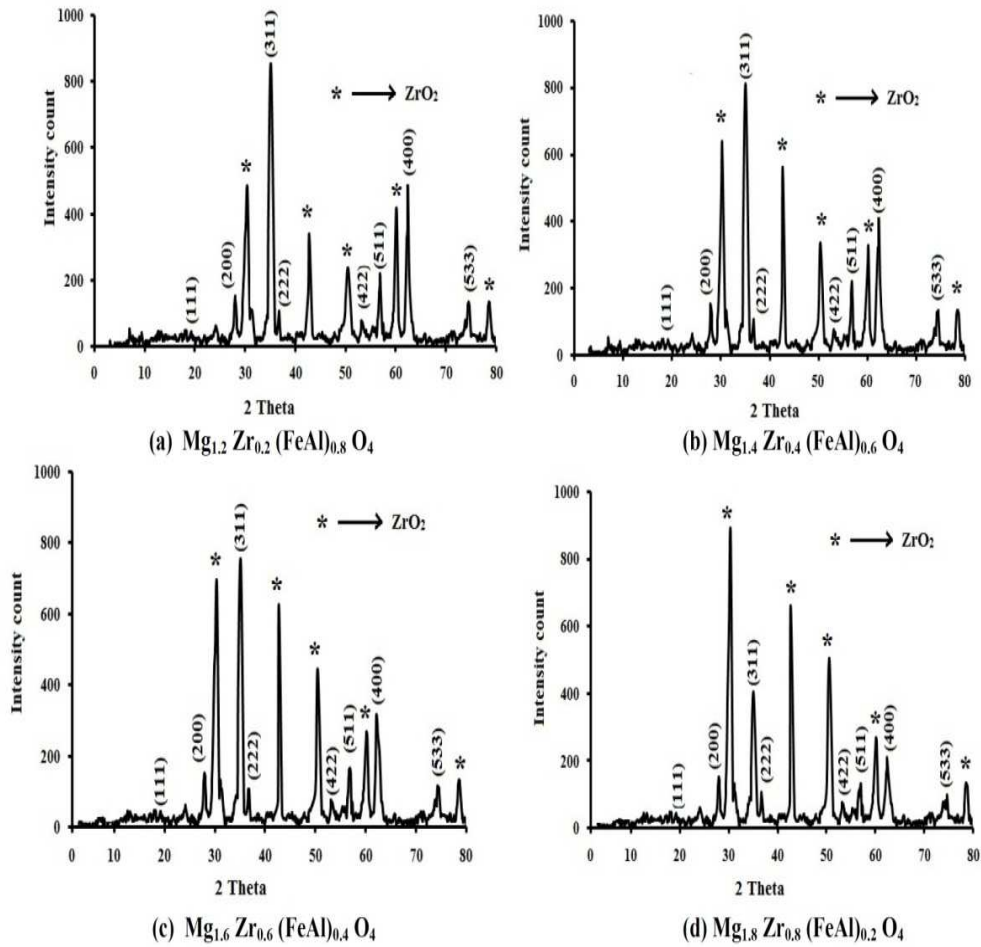


Figure 1: XRD of $Mg_{(1+x)}Zr_x(FeAl)_{1-x}O_4$

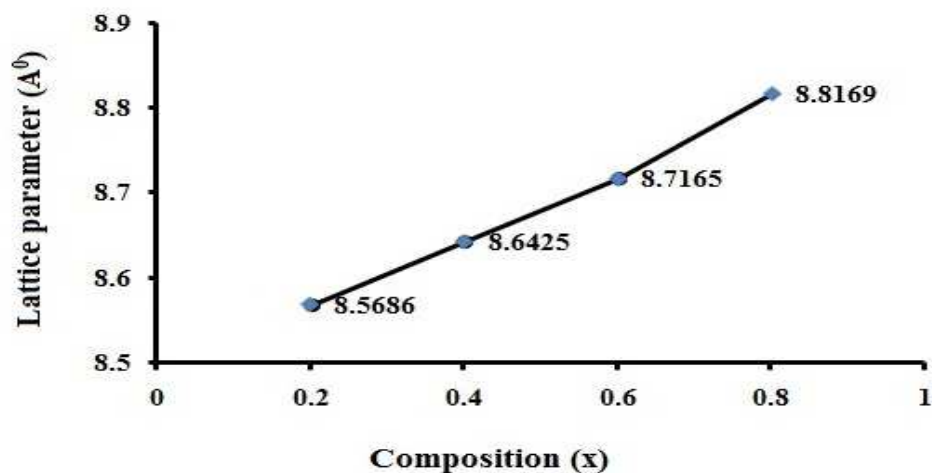


Figure 2: Variation of Lattices parameter

3.2. VSM (Vibrating Sample Magnetometer)

Figures 3 show the field dependent magnetization curves (M-H) of Zr and Al substituted Magnesium ferrites. Magnetization of all the compositions, at an applied magnetic field of 1.25 KG.m, is observed to attain saturation at room temperature. It is noted from the M-H curves the magnetization increases with the concentration of Zr⁴⁺ ions [15],[16]. The increasing coercivity indicating that the nature of material changes from superparamagnetic to ferromagnetic, therefore the magnetic moment increases (as shown in table 1). It is well known that the total magnetization in ferrites depends on the anti-parallel magnetic interaction between the magnetic moments of cations which are occupied in tetrahedral (A- site) and octahedral (B- site) respectively [17]. Since, the overall magnetization comes from the difference between the magnetization of the A and B sites respectively [18]. It is already discussed in the section 3.1. The Zr⁴⁺ ion occupies tetrahedral site therefore the magnetic moment of tetrahedral site is expected to decrease, which turns to enhance total magnetic moment with addition of Zr⁴⁺ ion substitution [19]. In the present research work chemical compositions of Mg_(1+x)Zr_x(FeAl)_{1-x}O₄ (where x = 0.2, 0.4, 0.6, 0.8) were used, here all the ions have zero magnetic moments except Fe³⁺ (5 μB). Therefore the net magnetization depends on the distribution of Fe³⁺ ions in A and B sites.

In the case of figure 3c, the magnetization increases in Mg_{1.6}Zr_{0.6}(FeAl)_{0.4}O₄ rapidly than in all other compositions, because the Fe³⁺ ions are totally occupied in octahedral sites and Zr⁴⁺ ions are totally occupied in tetrahedral sites. Therefore the anti-parallel magnetic interaction does not cancel out the magnetic moment on B sites (as shown in table 1) and which is the highest magnetic moment amongst all other chemical compositions. On the basis of the above explanation we have determined that Zr⁴⁺ ions help to increase and/or decrease the magnetization of the materials [20].

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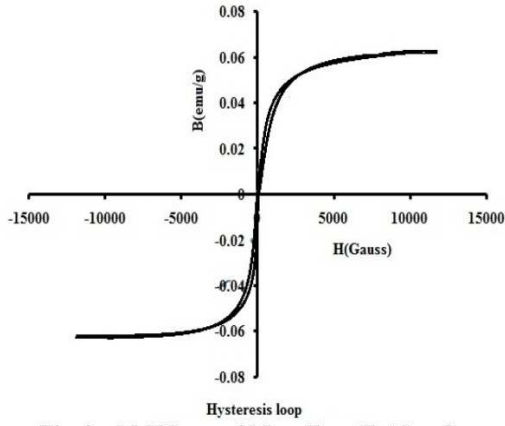


Fig. 3a M-H Loop of $Mg_{1.2}Zr_{0.2}(FeAl)_{0.8}O_4$

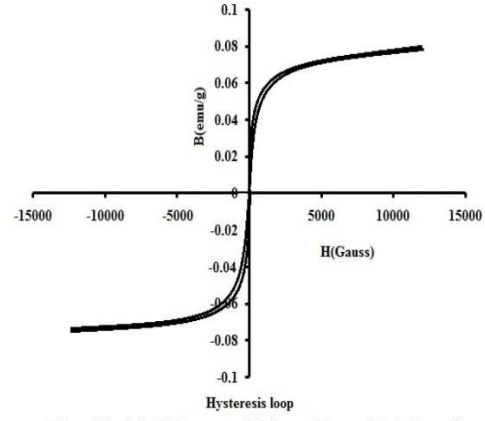


Fig. 3b M-H Loop of $Mg_{1.2}Zr_{0.4}(FeAl)_{0.6}O_4$

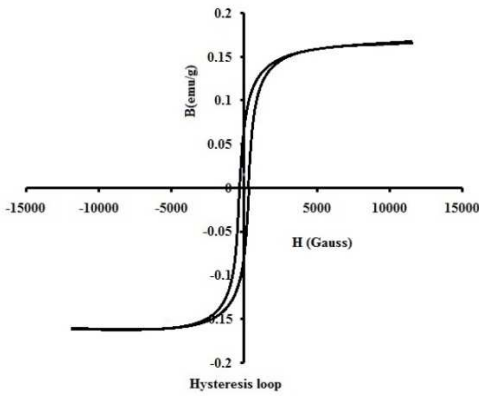


Fig. 3c M-H loop of $Mg_{1.2}Zr_{0.6}(FeAl)_{0.4}O_4$

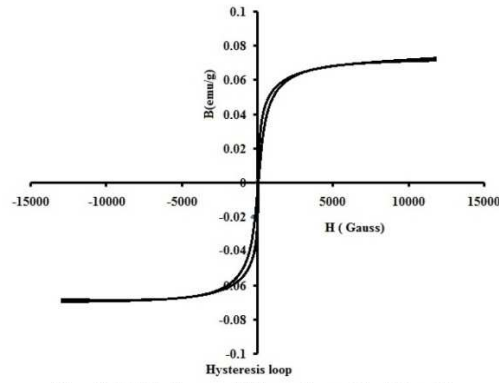


Fig. 3d M-h loop of $Mg_{1.2}Zr_{0.8}(FeAl)_{0.2}O_4$

Figure 3: B-H Curve of $Mg_{(1+x)}Zr_x(FeAl)_{1-x}O_4$

Samples	Saturation Magnetization (Ms) (emu/g)	Retentivity (Mr) (emu/g)	Coercivity (Hc) (Gauss)	Bohr magnetron (μ_B)/molecule
$Mg_{1.2}Zr_{0.2}(FeAl)_{0.8}O_4$	66×10^{-3}	4×10^{-3}	125	2.0995×10^{-3}
$Mg_{1.4}Zr_{0.4}(FeAl)_{0.6}O_4$	72×10^{-3}	30×10^{-3}	195	2.4177×10^{-3}
$Mg_{1.6}Zr_{0.6}(FeAl)_{0.4}O_4$	175×10^{-3}	80×10^{-3}	500	5.5671×10^{-3}
$Mg_{1.8}Zr_{0.8}(FeAl)_{0.2}O_4$	78×10^{-3}	6×10^{-3}	200	2.2904×10^{-3}

Table 1: Magnetic properties

4. Conclusion

The nano crystalline, $Mg_{(1-x)}Zr_x(FeAl)_{1-x}O_4$ spinel ferrite of different compositions (where $x = 0.2, 0.4, 0.6, 0.8$) were successfully synthesized by sol-gel auto combustion technique. The X-ray diffraction results showed the formation of polycrystalline spinel structure. The lattice constant gradually increases with increasing concentration of Zr^{4+} ion. From the VSM study we have found that the saturation magnetization (M_s) is maximum for $x = 0.6$ than that of $x = 0.2, 0.4, 0.8$. We have observed that, the magnetization in these ferrite varied due to ionic radius of various substitution and the site preferences of magnetic moment of Zr^{4+} and Fe^{3+} .

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